US010049784B2

(12) **United States Patent**
Al-Harthi et al.

(10) **Patent No.:** **US 10,049,784 B2**
(45) **Date of Patent:** **Aug. 14, 2018**

(54) **NANOCOMPOSITE FILMS WITH CONDUCTING AND INSULATING SURFACES**

(71) Applicant: **KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS**, Dhahran (SA)

(72) Inventors: **Mamdouh Ahmed Al-Harthi**, Dhahran (SA); **Osamah Awadh Bin-Dahman**, Dhahran (SA); **Mostafizur Rahaman**, Dhahran (SA)

(73) Assignee: **King Fahd University of Petroleum and Minerals**, Dhahran (SA)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 41 days.

(21) Appl. No.: **14/877,623**

(22) Filed: **Oct. 7, 2015**

(65) **Prior Publication Data**

US 2017/0103826 A1 Apr. 13, 2017

(51) **Int. Cl.**
H01B 1/24 (2006.01)
H01B 3/00 (2006.01)
(Continued)

(52) **U.S. Cl.**
CPC *H01B 3/004* (2013.01); *B29B 7/90* (2013.01); *B29C 39/02* (2013.01); *B32B 5/145* (2013.01);
(Continued)

(58) **Field of Classification Search**
CPC ... H01B 1/04; H01B 1/24; H01B 3/18; H01B 3/30–3/47; H01B 3/002–3/006
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,451,471 B1* 9/2002 Braun B29C 59/02
429/480
7,976,950 B2 7/2011 Okai et al.
(Continued)

FOREIGN PATENT DOCUMENTS

EP 113277 A * 7/1984
WO WO-2010102731 A1 * 9/2010 .... B29C 45/0013
(Continued)

OTHER PUBLICATIONS

NPL from HyperPhysics on Conductivity and Resistivity. Retrieved from http://hyperphysics.phy-astr.gsu.edu/hbase/electric/resis.html on Mar. 23, 2017.*
(Continued)

Primary Examiner — Z. Jim Yang
(74) *Attorney, Agent, or Firm* — Oblon, McClelland, Maier & Neustadt, L.L.P.

(57) **ABSTRACT**

Nanocomposite films comprising conductive nanofiller dispersed throughout a polymer matrix and further comprising at least two surfaces with differing amounts of filler and differing electrical resistivity values are provided. In particular, nanocomposites comprising polyvinyl alcohol as the polymer matrix and nanosheets and/or nanoplatelets of graphene as the conductive filler are provided. In addition, a process for forming the nanocomposites, methods for characterizing the nanocomposites as well as applications in or on electrical and/or electronic devices are provided.

10 Claims, 3 Drawing Sheets
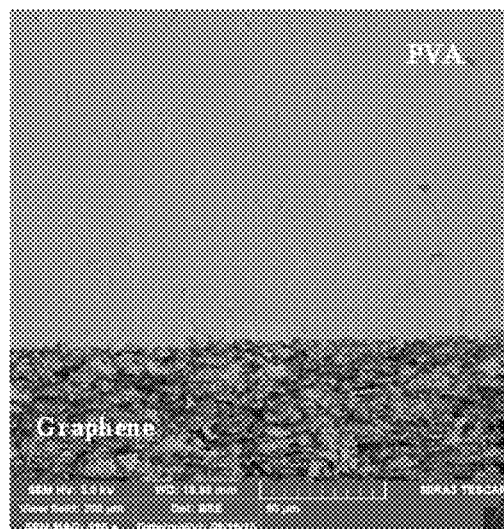
(51) **Int. Cl.**

H01B 1/04	(2006.01)
C08J 5/18	(2006.01)
B32B 27/06	(2006.01)
B32B 27/30	(2006.01)
B29B 7/90	(2006.01)
B29C 39/02	(2006.01)
B32B 5/14	(2006.01)
B29C 39/00	(2006.01)
B29K 29/00	(2006.01)
B29K 105/16	(2006.01)
B29K 507/04	(2006.01)
B29L 7/00	(2006.01)
B29L 31/34	(2006.01)

(52) **U.S. Cl.**

CPC *B32B 27/06* (2013.01); *B32B 27/306* (2013.01); *C08J 5/18* (2013.01); *H01B 1/04* (2013.01); *H01B 1/24* (2013.01); *B29C 39/003* (2013.01); *B29K 2029/04* (2013.01); *B29K 2105/162* (2013.01); *B29K 2507/04* (2013.01); *B29K 2995/0005* (2013.01); *B29L 2007/008* (2013.01); *B29L 2031/34* (2013.01); *B32B 2250/02* (2013.01); *B32B 2307/202* (2013.01); *B32B 2307/206* (2013.01); *B32B 2307/21* (2013.01); *B32B 2307/212* (2013.01); *B32B 2457/00* (2013.01); *B32B 2457/10* (2013.01); *B32B 2457/12* (2013.01); *B32B 2457/16* (2013.01); *B32B 2457/202* (2013.01); *B32B 2457/208* (2013.01); *C08J 2329/04* (2013.01)

(56) **References Cited**

U.S. PATENT DOCUMENTS

2007/0199729 A1*	8/2007	Siegel	....	C08K 3/22 174/73.1
2011/0024694 A1*	2/2011	Shah	....	C08J 5/042 252/502
2011/0088931 A1*	4/2011	Lettow	....	B82Y 30/00 174/257
2011/0253969 A1*	10/2011	Dai	....	B82Y 30/00 257/9
2012/0145315 A1*	6/2012	Knaapila	....	B82Y 30/00 156/273.9
2013/0187099 A1*	7/2013	Luethen	....	C08K 3/04 252/511
2014/0246220 A1*	9/2014	Allais	....	H01L 33/441 174/110 R
2014/0306164 A1*	10/2014	Restuccia	....	C08K 3/04 252/511

2015/0001448 A1*	1/2015	Wang	....	H01B 3/441 174/110 R
2015/0007885 A1*	1/2015	Hashimoto	....	H01L 31/049 136/256
2015/0073072 A1*	3/2015	Kim	....	H01L 33/447 524/106
2015/0284253 A1*	10/2015	Zhamu	....	C01B 31/043 423/448
2015/0300782 A1*	10/2015	Craig	....	F41H 5/0471 428/215
2015/0344643 A1*	12/2015	Al-Harthi	....	C08J 3/28 524/562
2016/0122497 A1*	5/2016	Al-Harthi	....	C08K 3/04 524/855
2016/0133361 A1*	5/2016	Logakis	....	C01B 31/043 174/135
2016/0155530 A1*	6/2016	Someya	....	A61L 27/50 174/257
2016/0326393 A1*	11/2016	Jung	....	H01B 1/24
2017/0121179 A1*	5/2017	Bepete	....	C01B 31/0273

FOREIGN PATENT DOCUMENTS

WO	WO 2014206435 A1 *	12/2014	....	C01B 31/043
WO	WO 2015008857 A1 *	1/2015	....	A61L 27/50

OTHER PUBLICATIONS

NPL on Reduced Graphene Oxide from Graphenea. Retrieved from https://www.graphenea.com/collections/graphene-oxide/products/reduced-graphene-oxide-1-gram.*

NPL from Machinery's Handbook, 27th edition. 2004, p. 416.*

Rathod, S. G., et al, "Thermal, Mechanical and Dielectric Properties of Poly(vinyl alcohol)/Graphene Oxide Composites", AIP Conference Proceedings, vol. 1591, p. 1769, (2014).

Zhao, X., et al., "Enhanced Mechanical Properties of Graphene-Based Poly(vinyl alcohol) Composites", Macromolecules, vol. 43, pp. 2357-2363, (2010).

Liang, J., et al., "Molecular-Level Dispersion of Graphene into Poly(vinyl alcohol) and Effective Reinforcement of their Nanocomposites", Advanced Functional Materials, vol. 19, pp. 1-6, (2009).

Cheng, H. K. F., et al., "Poly(vinyl alcohol) Nanocomposites Filled with Poly(vinyl alcohol)-Grafted Graphene Oxide", ACS Applied Materials & Interfaces, vol. 4, pp. 2387-2394, (2012).

Ahn, S.I., et al., "Reduction of Graphene Oxide Film with Poly (Vinyl Alcohol)", "Chemical Physics Letters", vol. 625, 1 Page total (Apr. 1, 2015) (Abstract only).

Traina, M., et al., "In Situ Reduction of Graphene Oxide Dispersed in a Polymer Matrix", Journal of Nanoparticle Research, vol. 14, No. 801, 6 Pages total, (Mar. 18, 2012).
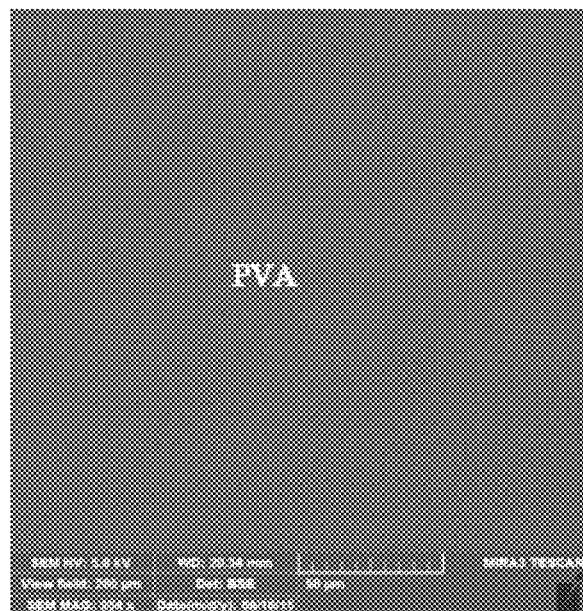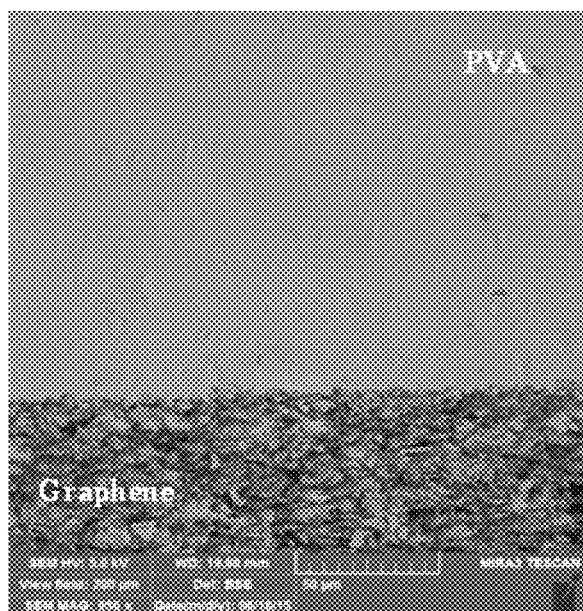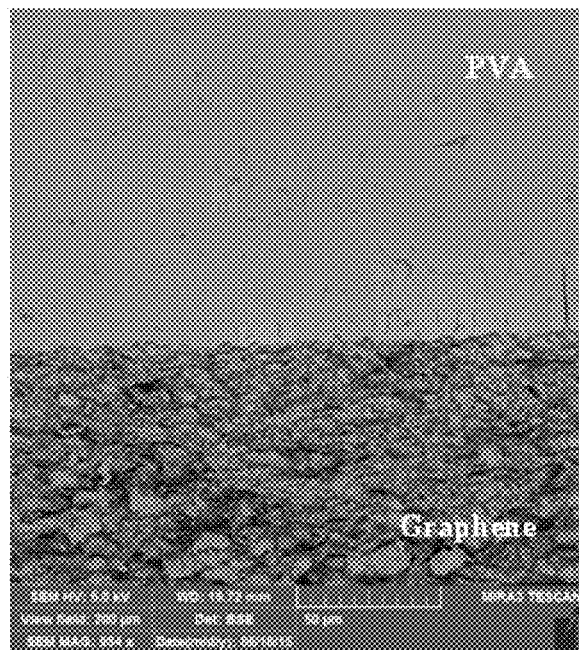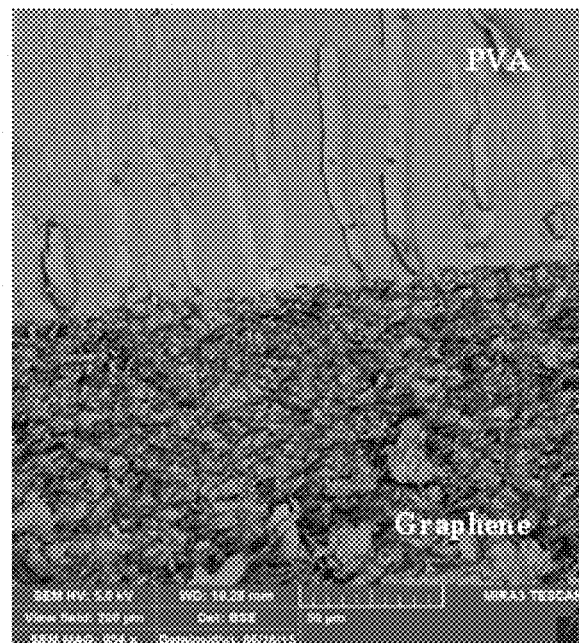
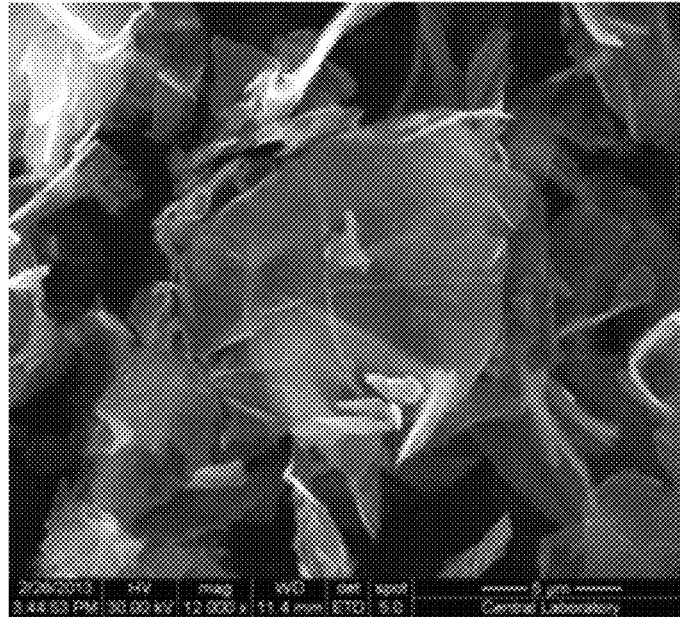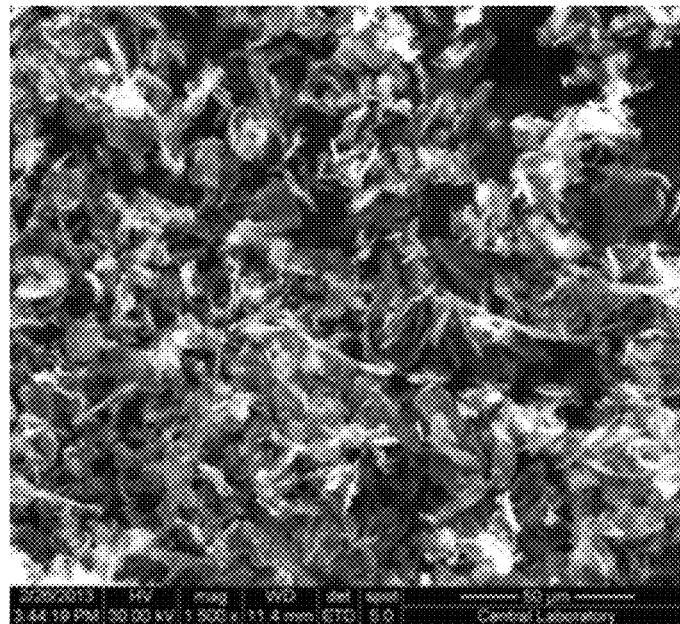* cited by examiner

FIG. 1A

FIG. 1B

FIG. 1C

FIG. 1D

FIG. 2A

FIG. 2B

NANOCOMPOSITE FILMS WITH CONDUCTING AND INSULATING SURFACES

BACKGROUND OF THE INVENTION

Technical Field

The present disclosure relates to a nanocomposite film comprising a polymer matrix and conductive nanofiller dispersed in the matrix having a first surface with a first resistivity and a second surface with a second resistivity, a process for producing the nanocomposite film and an electronic device comprising the nanocomposite film.

Description of the Related Art

The "background" description provided herein is for the purpose of generally presenting the context of the disclosure. Work of the presently named inventors, to the extent it is described in this background section, as well as aspects of the description which may not otherwise qualify as prior art at the time of filing, are neither expressly or impliedly admitted as prior art against the present invention.

Polymer composites filled by graphitic nanostructures have attracted significant attention as a result of their unique mechanical, electric and optical properties. Nano-scale conductive fillers can create a seamlessly interconnected percolative network within the polymer matrix altering the energy storing and transporting properties of the composite while reinforcing the native polymer and enhancing its mechanical strength.

Graphene is a two-dimensional arrangement of carbon atoms in a hexagonal lattice with sheets having a thickness of just one atom (0.33 nm). The graphene has a layered crystal structure, in which the carbon atoms are strongly bonded on a two-dimensional network consisting of hexagons. Graphene combines the layered structure of clays with the excellent mechanical, thermal and electrical properties of carbon nanotubes to provide unique functional properties in final products. Since the isolation of a single sheet of graphene [K. S. Novoselov, a K. Geim, S. V Morozov, D. Jiang, Y. Zhang, S. V Dubonos, I. V Grigorieva, a a Firsov, Science (80-.). 306 (2004) 666.—incorporated herein by reference in its entirety], graphene has attracted the attention of researchers pursuing novel nanocomposites [J. Liang, Y. Huang, L. Zhang, Y. Wang, Y. Ma, T. Guo, Y. Chen, Adv. Funct. Mater. 19 (2009) 2297.—incorporated herein by reference in its entirety].

In recent years, graphene has become a preferred nanofiller as a result of its unique characteristics. Graphene is known to be combined as a few layers (graphite) and different types of graphite nanoplatelets such as thermally expanded graphite, graphene oxide (GO) and chemically modified graphene have been used to make functional polymer nanocomposites [H. Kim, A. Abdala, C. W. Macosko, Macromolecules 43 (2010) 6515.; and C. Gómez-Navarro, J. C. Meyer, R. S. Sundaram, A. Chuvilin, S. Kurasch, M. Burghard, K. Kern, U. Kaiser, Nano Lett. 10 (2010) 1144.; and J. T. Robinson, F. K. Perkins, E. S. Snow, Z. Wei, P. E. Sheehan, Nano Lett. 8 (2008) 3137.; and Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, Adv. Mater. 22 (2010) 3906.—each incorporated herein by reference in its entirety]. The initial development of graphene from graphite was via acid treatment (Hummer's reaction) to exfoliate graphene sheets [W. S. Hummers, R. E. Offeman, J. Am. Chem. Soc. 80 (1958) 1339.—incorporated herein by reference in its entirety].

Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer that has been used in numerous applications includ-

ing water-soluble packaging films, drug delivery, paper coating, textile sizing, etc. PVA is well known for its biocompatibility and non-toxicity and can easily be blended with a wide range of natural polymers and fillers to make biodegradable composites with remarkable properties. Despite many studies, included below, describing several unique nanocomposites, there remain many possibilities for developing different types of graphitic nanocomposites with different morphologies and functionalization for enhancing a number of chemical, mechanical, and electrical properties and for use across industries and disciplines.

For example, Xu et al. [Y. Xu, W. Hong, H. Bai, C. Li, G. Shi, Carbon N. Y. 47 (2009) 3538.—incorporated herein by reference in its entirety] reported the preparation of a PVA/graphene oxide nanocomposite that was shown to be strong and ductile in comparison to the pristine polymer. Liang et al. [J. Liang, Y. Huang, L. Zhang, Y. Wang, Y. Ma, T. Guo, Y. Chen, Adv. Funct. Mater. 19 (2009) 2297.—incorporated herein by reference in its entirety] have also prepared PVA/graphene oxide nanocomposites by a simple solution mixing in water and casting method. The molecular level dispersion of graphene (only 0.7 wt % of graphene oxide) in the polymer matrix significantly improved the mechanical strength properties in comparison to the native polymer.

Furthermore, Cheng et al. [H. K. F. Cheng, N. G. Sahoo, Y. P. Tan, Y. Pan, H. Bao, L. Li, S. H. Chan, J. Zhao, ACS Appl. Mater. Interfaces 4 (2012) 2387.—incorporated herein by reference in its entirety] used PVA/graphene/graphene oxide instead of pristine graphene oxide alone to further improve the properties of PVA nanocomposites. The results showed a 88% increase in tensile strength, a 150% increase in Young's modulus and a 225% increase in elongation at break compared to the native polymer with only a 1% by weight loading of filler. Zhao et al. [X. Zhao, Q. Zhang, D. Chen, P. Lu, Macromolecules 43 (2010) 2357.—incorporated herein by reference in its entirety] prepared a staple dispersion of graphene oxide in water with the aid of sodium dodecyl benzene sulfonate (SDBS) via sonication. The results demonstrated a 150% increase in tensile strength with the addition of 1.8% by weight graphene to the native polymer.

In addition, Huang et al. [H.-D. Huang, P.-G. Ren, J. Chen, W.-Q. Zhang, X. Ji, Z.-M. Li, J. Memb. Sci. 409 (2012) 156.—incorporated herein by reference in its entirety] prepared PVA/graphene oxide nanosheet composites by a simple solution mixing process. A significant change was noted in the barrier property and the results lead to applications in the packaging industry. Wang et al. [C. Wang, Y. Li, G. Ding, X. Xie, M. Jiang, J. Appl. Polym. Sci. 127 (2013) 3026.—incorporated herein by reference in its entirety] reported the characterization and preparation of PVA/graphene oxide nanocomposites via electrospinning methods. The results showed a decrease in decomposition temperature as well as a significant increase (42×) in tensile strength with a very low loading (0.02 wt. % of graphene oxide) in the PVA matrix.

Recently, Ye et al. [Y.-S. Ye, M.-Y. Cheng, X.-L. Xie, J. Rick, Y.-J. Huang, F.-C. Chang, B.-J. Hwang, J. Power Sources 239 (2013) 424.—incorporated herein by reference in its entirety] demonstrated significant improvements in ionic conductivity and methanol crossover for a PVA membrane reinforced with graphene leading to fuel cell applications. Ma et al. [H.-L. Ma, Y. Zhang, Q.-H. Hu, S. He, X. Li, M. Zhai, Z.-Z. Yu, Mater. Lett. 102-103 (2013) 15.—incorporated herein by reference in its entirety] prepared nanocomposite films of PVA and a glucose-reduced graphene oxide (rGO) by a solution blending method. The

aqueous suspension stability of rGO was investigated by adding sodium dodecyl benzene sulfonate (SDBS) and poly (N-vinyl-2-pyrrolidone) (PVP). The results showed that PVP enhanced the dispersion of rGO in water significantly better than SDBS. Furthermore, the results showed an increased tensile strength and an increased Young's modulus for the nanocomposite films compared to the native PVA polymer.

In view of the forgoing, one aspect of the present disclosure is to design and provide nanocomposites with a non-uniform and controlled dispersion of conductive nanofillers in a polymeric matrix to introduce electrical conductivity. It is envisioned that by this manner nanocomposites having the same or different local and bulk electrical resistivities can be produced. It will be advantageous to design nanocomposites and processes for economically producing those nanocomposites that efficiently and economically provide a single material having portions and surfaces that function as a conductor, semiconductor or insulator and mixtures thereof in contrast to the bulk material or other portions and surfaces. Furthermore, the present disclosure envisions widespread applications of such materials throughout the disciplines that employ electronic devices.

BRIEF SUMMARY OF THE INVENTION

According to a first aspect, the present disclosure relates to a nanocomposite film comprising i) a polymer matrix ii) a conductive nanofiller dispersed in the matrix iii) a first surface having a first content of conductive nanofiller and a first resistivity and iv) a second surface having a second content of conductive nanofiller and a second resistivity, wherein the second content of conductive nanofiller is greater than or equal to the first content of conductive nanofiller and wherein the second resistivity is less than or equal to the first resistivity.

In one embodiment, the nanocomposite film comprises up to 25 weight percent of the conductive nanofiller relative to the total weight of the nanocomposite film.

In one embodiment, the nanocomposite film has an average thickness of 0.1-1.0 mm.

In one embodiment, the polymer matrix comprises polyvinyl alcohol.

In one embodiment, the conductive nanofiller comprises graphene.

In one embodiment, the graphene is in the form of nanosheets having an average longest dimension of 1-75 μm and an average thickness of 0.5-300 nm or nanoplatelets having an average diameter of 1-75 μm and an average thickness of 0.5-300 nm.

In one embodiment, the nanocomposite film comprises from 0.01-0.25 weight percent of the conductive nanofiller relative to the total weight of the nanocomposite film.

In one embodiment, the nanocomposite film comprises from 0.5-1.0 weight percent of the conductive nanofiller relative to the total weight of the nanocomposite film.

In one embodiment, the nanocomposite film comprises from 3-10 weight percent of the conductive nanofiller relative to the total weight of the nanocomposite film.

In one embodiment, the first surface is insulating and the second surface is insulating.

In one embodiment, the first surface is insulating and has a first resistivity of greater than 10^8 ohm·cm^2.

In one embodiment, the second surface is insulating and has a second resistivity of greater than 10^8 ohm·cm^2.

In one embodiment, the first surface is insulating and the second surface is antistatic.

In one embodiment, the second surface is antistatic and has a second resistivity of 10^4-10^8 ohm·cm^2.

In one embodiment, the first surface is insulating and the second surface is semiconducting and/or conducting.

In one embodiment, the second surface is semiconducting and/or conducting and has a second resistivity of less than 10^4 ohm·cm^2.

According to a second aspect, the present disclosure relates to a process for forming the nanocomposite film comprising i) sonicating a solution of conductive nanofiller to form a stable dispersion of nanofiller ii) mixing the dispersion of nanofiller with a solution of polymer to form a reaction mixture and iii) casting the reaction mixture and drying to form the nanocomposite film.

In one embodiment, the polymer comprises polyvinyl alcohol.

In one embodiment, the conductive nanofiller comprises graphene.

According to a third aspect, the present disclosure relates to an electronic device comprising the nanocomposite film, wherein the nanocomposite film is present in or on said electronic device.

The foregoing paragraphs have been provided by way of general introduction, and are not intended to limit the scope of the following claims. The described embodiments, together with further advantages, will be best understood by reference to the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the disclosure and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

FIG. 1A is a field emission scanning electron microscopy (FESEM) image of a control pure polyvinyl alcohol (PVA) film.

FIG. 1B is a FESEM image of the prepared nanocomposite film wherein the conductive nanofiller is graphene and the matrix is polyvinyl alcohol comprising 5 weight percent of graphene relative to the total weight of the nanocomposite film.

FIG. 1C is a FESEM image of the prepared nanocomposite film wherein the conductive nanofiller is graphene and the matrix is polyvinyl alcohol comprising 7 weight percent of graphene relative to the total weight of the nanocomposite film.

FIG. 1D is a FESEM image of the prepared nanocomposite film wherein the conductive nanofiller is graphene and the matrix is polyvinyl alcohol comprising 10 weight percent of graphene relative to the total weight of the nanocomposite film.

FIG. 2A is a scanning electron microscopy (SEM) image of the magnified view of the graphene as purchased from Grafen Chemical Industries Co.

FIG. 2B is a scanning electron microscopy (SEM) image of the graphene as purchased from Grafen Chemical Industries Co.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Referring now to the drawings.

According to a first aspect, the present disclosure relates to a nanocomposite film including a polymer matrix and conductive nanofiller dispersed in the matrix.

As used herein, "composite" refers to a combination of two or more distinct constituent materials into one. The individual components, on an atomic level, remain separate and distinct within the finished structure. The materials may have different physical or chemical properties, that when combined, produce a material with characteristics different from the original components. A composite is understood to consist of a bulk phase, termed the matrix, enclosing a reinforcing phase, termed the filler.

Nanocomposites are nanomaterials where a nano-object is dispersed into a matrix or phase. A nanocomposite is a multiphase solid material where one of the phases, the nano-object, has one, two or three dimensions of less than 100 nm, or structures having nano-scale repeat distances between the different phases that make up the material. In the broadest sense this definition can include porous media, colloids, gels and copolymers, but is more usually taken to mean the solid combination of a bulk matrix and one or more nanodimensional filler phases differing in properties due to dissimilarities in structure and chemistry. In general, the mechanical, electrical, thermal optical, electrochemical and catalytic properties of the nanocomposite will differ from that of the component materials.

Nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the filler phase and/or its exceptionally high aspect ratio. The aspect ratio of a nanofiller is defined as the length of the major (long) axis divided by the width of the minor (short) axis. The area of interface between matrix and filler phase or phases is typically an order of magnitude greater than for conventional composite materials.

A polymer nanocomposite is a multiphase system consisting of a polymer or copolymer having nanofillers dispersed in the polymer matrix. These nanofillers may be of different shapes and sizes and comprise particles, sheets and/or fibers, but at least one dimension must be in the range of less than 100 nm. Appropriately adding nanomaterial to a polymer matrix can enhance its performance by capitalizing on the nature and properties of the nanoscale filler. This strategy is particularly effective in yielding high performance composites when the properties of the nanoscale filler are substantially different or better than those of the matrix. Nanoscale dispersion of filler or controlled nanostructures into a composite can introduce new physical properties and novel behaviors that are absent in the unfilled matrices, effectively changing the nature of the original matrix.

A polymer is a large molecule, or macromolecule, composed of many repeated subunits. Polymers, both natural and synthetic are created via polymerization of many small molecules, termed monomers. When two or more different monomers unite together to polymerize it is termed a copolymer and the process is termed copolymerization. The consequently large molecular mass of polymers relative to small molecule compounds produce unique physical properties including toughness, viscoelasticity, and a tendency to form semicrystalline structures rather than crystals. The polymer of the polymer matrix of the present disclosure may be a homopolymer (one monomer) or a copolymer (more than one monomer) and mixtures thereof.

Copolymers can be classified based on how their constituent monomeric units are arranged along the chain. Alternating copolymers have regular alternating monomeric units. Periodic copolymers have monomeric units arranged in a repeating sequence. Statistical copolymers have a sequence of monomer residues following a statistical rule. Random copolymers have the probability of finding a given type of monomer unit at a particular point in the chain equal to the mole fraction of that monomer in the chain. Block copolymers comprise two or more homopolymer subunits linked by covalent bonds and may require an intermediate non-repeating subunit or junction block. In gradient copolymers the monomer composition changes gradually along the chain. The polymer of the polymer matrix of the present disclosure may be a homopolymer, an alternating copolymer, a periodic copolymer, a statistical copolymer, a block copolymer, a gradient copolymer or mixtures thereof.

Polymers can be classified based on their origin and occurrence in nature. Polymers which occur in nature are called natural polymers, also known as biopolymers. Examples of such polymers include, but are not limited to natural rubber, natural silk, shellac, amber, cellulose, starch, alginate, chitosan, collagen, keratin, gelatin, fibrin, polypeptides, polysaccharides, nucleic acids, proteins, etc. Semisynthetic polymers are chemically modified natural polymers and include hydrogenated natural rubber, cellulosic, cellulose nitrate, methyl cellulose, etc. A polymer which has been synthesized in a laboratory is known as a synthetic polymer or manmade polymers. Examples of such polymers include synthetic rubber, polyvinyl alcohol, polyethylene, polyethylene glycol, polystyrene, polyvinyl chloride (PVC or vinyl), polypropylene, polyacrylonitrile, polyvinyl burtyral (PVB), polysulfone, polycapro lactone (PCL), polyglycerol sebacate (PGS), poly(lactic-co-glycolic acid), phenol formaldehyde resin (Bakelite), neoprene, nylon, silicone etc. The polymer of the polymer matrix of the present disclosure may be a natural polymer, a semisynthetic polymer or a synthetic polymer or copolymers and mixtures thereof.

Polymers can be classified based on their thermal response. Thermoplastic polymers can be softened or plasticized repeatedly upon the application of thermal energy without much change in properties if treated with certain precautions. Examples of such polymers include polyolefins, nylons, linear polyesters and polyethers, poly(vinyl chloride), sealing wax, etc. Thermosetting polymers undergo certain chemical changes on heating and convert themselves into an infusible mass. The curing or setting process involves chemical reaction leading to further growth and cross linking of the polymer chain molecules and producing giant molecules. Examples of such polymers include phenolic resins, urea, epoxy resins, diene rubbers, etc. The polymer of the polymer matrix of the present disclosure may be a thermoplastic polymer, a thermosetting polymer or copolymers and mixtures thereof.

Polymers can be classified based on their mode of formation. Addition polymers are formed from olefinic, diolefinic, vinyl and related monomers. They are formed from simple addition of monomer molecules to each other in quick succession by a chain mechanism. This process is called addition polymerization. Examples of such polymers include polyethylene, polypropylene, polystyrene. Condensation polymers are formed from intermolecular reactions between bifunctional or polyfunctional monomer molecules having reactive functional groups such as —OH, —COOH, —NH$_2$, —NCO, etc. The polymer of the polymer matrix of the present disclosure may be an addition polymer, a condensation polymer or copolymers and mixtures thereof.

Polymers can be classified based on their structure or line structure. If the monomer units are joined in a linear fashion the polymer is said to be a linear polymer. If the monomer units are joined in a branched manner the polymer is said to be a branched polymer. If the monomer units are joined together in a chain fashion the polymer is said to be a cross linked polymer. A graft copolymer is a special type of branched copolymer where the side chains are structurally

distinct from the main chain. The individual chains of a graft copolymer may be homopolymers or copolymers. The polymer of the polymer matrix of the present disclosure may be a linear homopolymer (one monomer), a linear copolymer (more than one monomer), a branched homopolymer, a branched copolymer, a cross linked homopolymer, a cross linked copolymer, a graft copolymer or mixtures and copolymers thereof.

Polymers can be classified based on their application and physical properties depending on the ultimate form and use of the polymer. Rubbers (elastomers) are high molecular weight polymers with long flexible chains and weak intermolecular forces. They typically exhibit tensile strength in the range of 300-3000 psi and elongation at break in the range of 300-1000% and examples include natural and synthetic rubber. Plastics are relatively tough substances with high molecular weight that can be molded with (or without) the application of heat. These are usually much stronger than rubbers. They typically exhibit tensile strength in the range of 4000-15000 psi and elongation at break in the range of 20-200% and examples include polyethylene, polypropylene, poly(vinyl chloride), polystyrene, etc. Fibers are long chain polymers characterized by highly crystalline regions resulting mainly from secondary forces. They have a much lower elasticity than plastics and elastomers. They typically also have high tensile strength ranging between 20,000-150,000 psi, are light weight and possess moisture absorption properties. The polymer of the polymer matrix of the present disclosure may be a rubber, a plastic, a fiber or copolymers and mixtures thereof.

Polymers can be classified based on their tacticity or structure. Tacticity may be defined as the geometric arrangement (orientation) of the characteristic group (side group) of monomer units with respect to the main chain (backbone) of the polymer. An isotactic polymer is the type of polymer in which the characteristic groups are arranged on the same side of the main chain. A syndiotactic polymer is the type of polymer in which the characteristic groups are arranged in an alternating fashion. An atactic polymer is the type of polymer in which the characteristic groups are arranged in irregular fashion (randomness) around the main chain. The polymer of the polymer matrix of the present disclosure may be isotactic, syndiotactic, atactic or copolymers and mixtures thereof.

Fillers are particles added to materials, such as polymers, to engender advantageous properties to the mixed material. Furthermore, fillers may affect the process by which a material or mixed material is processed, making production more efficient or more facile. In terms of the present disclosure the term "nanofiller" refers to added materials with at least one dimension of less than 100 nm that change the properties of the material to which they are added, or affect the process by which the mixed material is produced or manufactured. The nanofiller of the present invention may be selected from the group including, but not limited to, metallic, metal oxide, metal carbonate, ceramic, polymeric and carbonaceous nanomaterials.

In one embodiment, the nanofiller of the present disclosure may be of any shape that provides desired polymerization activity and desired properties in the resulting polymer/ nanofiller nanocomposite. The nanocomposites can be classified according to their nanofillers. One-dimensional nanofillers have one dimension of less than 100 nm, generally thickness. Examples of one-dimensional nanofillers include nanosheets, nanoplatelets, nanolaminas and nanoshells. Two-dimensional nanofillers have two dimensions of less than 100 nm, generally including diameter.

Examples of two-dimensional nanofillers include nanotubes, nanofibers and nanowhiskers. Three-dimensional nanofillers have all dimensions of less than 100 nm, and generally encompass isodimensional nanoparticles. Examples of three-dimensional nanofillers include nanoparticles, nanogranules and nanometric silica beads. The nanofiller of the present disclosure may be one-dimensional, two-dimensional, three-dimensional or mixtures thereof.

As used herein, the nanofiller or nanoparticle is defined as a small object that behaves as a whole unit with respect to its transport and properties having at least one dimension of less than 100 nm. Nanoparticles are named for the real-world shapes that they appear to represent. These morphologies sometimes arise spontaneously as an effect of the synthesis or from the innate crystallographic growth patterns of the materials themselves. Some of these morphologies may serve a purpose, such as bridging an electrical junction.

In one embodiment, the nanofiller of the present invention may be synthesized and formed into a variety of morphologies and forms including, but not limited to, nanoparticles, nanosheets, nanoplatelets, nanocrystals, nanospheres, nanowires, nanofibers, nanoribbons, nanorods, nanotubes, nanocylinders, nanogranules, nanowhiskers, nanoflakes, nanofoils, nanopowders, nanoboxes, nanostars, tetrapods, nanobelts, nanoflowers, etc. and mixtures thereof.

Nanofiller and nanocomposite characterization is necessary to establish understanding and control of nanoparticle and nanocomposite synthesis, assembly and application. In one embodiment, the nanofiller and nanocomposite are characterized by at least one technique. In another embodiment, it is envisioned that characterization is done using a variety of other techniques. Exemplary techniques include, but are not limited to, electron microscopy (TEM, SEM), atomic force microscopy (AFM), dynamic light scattering (DLS), X-ray photoelectron spectroscopy (XPS), X-ray fluorescence (XRF), powder X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF), ultraviolet-visible spectroscopy, Rutherford backscattering spectrometry (RBS), dual polartization interferometry and nuclear magnetic resonance (NMR).

In one embodiment, the nanofiller of the present disclosure is a conductive nanofiller. A conductive nanofiller refers to any nanometer sized material that is, or contains at least one material that is, electronically conductive i.e. has a non-zero flow of internal electric charges.

An electrical conductor is an object or type of material that allows the flow of electrical current in one or more directions. Metals, such as copper, typify conductors. Traditionally, most metals are good electrical conductors, most non-metals are not. In metals, the movable charged particles are electrons, but positive charges may also be mobile. Conductor implies that the outer electrons of the atoms are loosely bound and free to move through the material.

A semiconductor material has an electrical conductivity value falling between that of a conductor and an insulator. Semiconducting materials exist in two types, elemental materials and compound materials. The properties of a semiconductor rely on the unique arrangement of the crystal lattice and the movement of electrons and holes within the crystal lattice. Current conduction in a semiconductor occurs through the movement of free electrons and "holes", known collectively as charge carriers. Adding impurity atoms to a semiconducting material ("doping") can greatly increase the number of charge carriers within it.

An antistatic material or dissipative material is one which prevents, inhibits, eliminates, or reduces the accumulation of static electricity. In antistatic or dissipative materials the initial charges are suppressed (antistatic) or there is no or low initial charges (dissipative) and discharge to or from human contact is prevented. They represent a slight or minimum amount of conductivity that prevents the buildup of electric charge by dissipating or promoting the decay of the static electricity.

An electrical insulator is a material whose internal electric charges do not flow freely, and therefore make it very hard to conduct an electric current under the influence of an electric field. Most non-metallic solids are said to be good insulators, having very high resistance to the flow of charge through them. Most atoms hold on to their electrons tightly and are insulators. The property that distinguishes an insulator is its resistivity; insulators have higher resistivity than semiconductors or conductors.

Electrical resistivity (resistivity, specific electrical resistance or volume resistivity) is an intrinsic property that quantifies how strongly a given material opposes the flow of electric current. A low resistivity indicates that a material readily allows the movement of electric charge. Electrical conductivity (specific conductance) is the reciprocal of electrical resistivity, and measures a material's ability to conduct an electric current. As used in the present disclosure, an insulator is a material having a resistivity of greater than 10^8 ohm·cm^2, preferably in the range of 10^8-10^{17} ohm·cm^2, a semiconductor and/or conductor is a material having a resistivity of less than 10^4 ohm·cm^2, preferably less than 0.5×10^4 ohm·cm^2 and a antistatic material is a material having an intermediate resistivity in the range of 10^4-10^8 ohm·cm^2, preferably 10^5-10^8 ohm·cm^2.

According to its first aspect, the present disclosure relates to a nanocomposite film further including a first surface and a second surface. The first surface has a first content of conductive nanofiller and a first resistivity. The second surface has a second content of conductive nanofiller and a second resistivity. Additionally, the second content of conductive nanofiller is greater than or equal to the first content of conductive nanofiller, and the second resistivity is less than or equal to the first resistivity.

The nanocomposite film of the present disclosure may have various shapes and sizes. In one embodiment, the nanocomposite film may be horizontally oriented with a longitudinal axis. The first surface and second surface may be parallel to each other and the longitudinal axis. The first and second surface may also be opposing across the longitudinal axis and the vertical distance between the first surface and second surface may define the thickness of the nanocomposite film. In one embodiment, the film is double sided and the first and second surface are not adjoining. In terms of the present disclosure, the conductive nanofiller may be oriented parallel to the longitudinal axis, perpendicular to the longitudinal axis, or in orientations that are not exactly parallel or perpendicular to the longitudinal axis.

In a preferred embodiment, the conductive nanofiller of the second surface may be in such a quantity and dispersed in such a manner to effectively form one or more seamlessly interconnected infinite conductive networks. Percolation threshold refers to a mathematical concept related to the formation of long-range connectivity in random systems. Below the threshold a giant connected component does not exist; while above it, there exists a giant component of the order of the system size. In one embodiment, the second surface of the nanocomposite film of the present disclosure has a percolation threshold of less than less 10% conductive

nanofiller by weight relative to the total weight of the nanocomposite film, preferably less than 7%, preferably less than 5%, more preferably less than 3%.

As used herein, "surface" refers to the outermost part or most outside layer or boundary of a material, here the nanocomposite film. It includes both a continuous set of points with length and width providing an exterior face to the nancomposite and also may have a thickness and depth and be described as a layer. A surface, as used herein, is in complete and continuous contact with an external environment of the nanocomposite film of the present disclosure as well as the nanocomposite film itself. In one embodiment, the nanocomposite film of the present disclosure comprises a first and second surface. It is further envisaged that the present disclosure may be adapted to incorporate a third surface, a fourth surface, a fifth surface, etc. or a plurality of surfaces with defined content of nanofiller and defined electrical resistivity.

As used herein, "core" refers to the portion of the nanocomposite that is neither the first surface nor the second surface. The core may have characteristics of the first surface, the second surface, both and/or neither. In a preferred embodiment, the first and second surface form distinct layers with distinct and identifiable interfaces between the two surfaces or each surface and the nanocomposite core. In one embodiment, the first and second surfaces form distinct layers, although the interface between the two surfaces or each surface and the nanocomposite core is a mixture of both the first and second surface, a mixture of the first surface and the nanocomposite core, a mixture of the second surface and the nanocomposite core, or a mixture of the first surface, the second surface and the nanocomposite core. The nanocomposite film described herein is singular comprising a first surface, a second surface, a core and their interfaces. The film is not formed by conjoining multiple films and has no internal film-to-film interfaces.

In one embodiment, the core of the nanocomposite film may have a conductive nanofiller content gradient. Generally, the core will have a content of conductive nanofiller greater than the first surface and less than the second surface. In one embodiment, the content of the conductive nanofiller in the core may increase at greater distances from the first surface and smaller distances towards the second surface. Conversely, the content of conductive nanofiller in the core may decrease at greater distances from the second surface and smaller distances towards the first surface.

In one embodiment, the nanocomposite film has up to 25% conductive nanofiller by weight relative to the total weight of the nanocomposite film, preferably up to 20%, preferably up to 15%, preferably up to 10%, preferably up to 9%, preferably up to 8%, preferably up to 7%, preferably up to 6%, preferably up to 5%, preferably up to 4%, preferably up to 3%, preferably up to 2%, preferably up to 1%, preferably up to 0.75%, preferably up to 0.5%, preferably up to 0.25%, preferably up to 0.2%, preferably up to 0.15%, preferably up to 0.1%, preferably up to 0.01%.

In one embodiment, the nanocomposite film is at least 75% polymer matrix by weight relative to the total weight of the nanocomposite film, preferably at least 80%, preferably at least 85%, preferably at least 90%, preferably at least 91%, preferably at least 92%, preferably at least 93%, preferably at least 94%, preferably at least 95%, preferably at least 96%, preferably at least 97%, preferably at least 98%, preferably at least 99%, preferably at least 99.5%, preferably at least 99.75%.

In one embodiment, the first surface has less than 50% of the total mass of conductive nanofiller in the nanocomposite

film, preferably less than 40%, preferably less than 30%, preferably less than 25%, preferably less than 20%, preferably less than 15%, preferably less than 10%, preferably less than 5%.

In one embodiment, the second surface has greater than 50% of the total mass of conductive nanofiller in the nanocomposite film, preferably greater than 60%, preferably greater than 70%, preferably greater than 75%, preferably greater than 80%, preferably greater than 85%, preferably greater than 90%, preferably greater than 95%.

In one embodiment, the nanocomposite film of the present disclosure has a total average thickness of 0.1-1.0 mm, preferably 0.2-0.8 mm, preferably 0.3-0.7 mm, preferably 0.4-0.6 mm or about 0.5 mm.

In one embodiment, the first surface of the present disclosure may encompass up to 70% of the total thickness of the nanocomposite film, preferably up to 60%, preferably up to 50%, preferably up to 40%, preferably up to 30%, preferably up to 25%, preferably up to 20%, preferably up to 15%, preferably up to 10%, preferably up to 5% of the total thickness of the nanocomposite film.

In one embodiment, the first surface of the present disclosure has a total average thickness of up to 0.5 mm, preferably up to 0.4 mm, preferably up to 0.3 mm, preferably up to 0.25 mm, preferably up to 0.2 mm, preferably up to 0.15 mm, preferably up to 0.1 mm, preferably up to 0.05 mm.

In one embodiment, the second surface of the present disclosure may encompass up to 70% of the total thickness of the nanocomposite film, preferably up to 60%, preferably up to 50%, preferably up to 40%, preferably up to 30%, preferably up to 25%, preferably up to 20%, preferably up to 15%, preferably up to 10%, preferably up to 5% of the total thickness of the nanocomposite film.

In one embodiment, the second surface of the present disclosure has a total average thickness of up to 0.5 mm, preferably up to 0.4 mm, preferably up to 0.3 mm, preferably up to 0.25 mm, preferably up to 0.2 mm, preferably up to 0.15 mm, preferably up to 0.1 mm, preferably up to 0.05 mm.

The mechanical properties of the nanocomposite film of the present disclosure are also of interest. Tensile strength is the maximum stress that a material can withstand while being stretched or pulled before failing or breaking. Young's modulus (tensile modulus, E-modulus or elastic modulus) is a measure of a material's stiffness or its resistance to being deformed elastically (non-permanently) when a force is applied and can be thought of as the ratio of stress to strain. In one embodiment, the nanocomposite film of the present disclosure has a tensile strength in the range of 5-75 MPa, more preferably 10-60 MPa, more preferably 15-50 MPa. The inclusion of nanofiller may increase the tensile strength by at least 20%. In one embodiment, the nanocomposite film of the present disclosure has a Young's modulus in the range of 2-80 MPa, preferably 10-70 MPa, preferably 15-60 MPa, more preferably 20-50 MPa. The inclusion of nanofiller may increase the tensile strength by at least 15%.

In a preferred embodiment, the polymer matrix is polyvinyl alcohol (PVA). Polyvinyl alcohol (PVA, PVOH or PVAl) is a water-soluble synthetic polymer. It has the idealized chemical formula $[CH_2CH(OH)]_n$. Polyvinyl alcohol, like most polymers, is an electrical insulator. It is white (colorless) and odorless, exhibits crystallinity and can be supplied as beads or as solutions in water. PVA is biocompatible, non-toxic, resistant to oil, grease and solvents and has a high tensile strength and flexibility. Additionally, PVA has excellent film forming, emulsifying and adhesive properties.

Polyvinyl alcohol (PVA) has a relatively simple chemical structure with a pendant hydroxyl group. Unlike most vinyl polymers, PVA is not prepared by polymerization of the corresponding monomer. The monomer, vinyl alcohol, does not exist in a stable form, but rather rearranges to its tautomer, acetaldehyde. PVA instead is prepared by the polymerization of vinyl acetate to polyvinyl acetate (PVAc), followed by hydrolysis of PVAc to PVA. Other precursor polymers are sometimes used, with formate or chloroacetate groups instead of acetate. The conversion of the polyesters is usually conducted by base-catalyzed transesterification with ethanol. The hydrolysis reaction does not go to completion resulting in polymers with a certain degree of hydrolysis that depends on the extent of the reaction. In essence, PVA is always a copolymer of PVA and PVAc.

Polyvinyl alcohol is an atactic material, defined as a macromolecule where the substituents are placed randomly along the chain. The percentage of meso diads is between 1 and 99%. In terms of microstructure, it is composed mainly of 1,3-diol linkages $[—CH_2—CH(OH)—CH_2—CH(OH)—]$ but a few percent of 1,2 diols $[—CH_2—CH(OH)—CH(OH)—CH_2-]$ occur, depending on the conditions for the polymerization of the vinyl ester precursor.

Several properties of the polyvinyl alcohol polymer depend on the amount of residual ester groups. The content of acetate groups, or degree of hydrolysis, has an effect on the chemical properties, solubility and crystallizability of PVA. Residual hydrophobic acetate groups weaken the intra- and intermolecular hydrogen bonding of adjoining hydroxyl groups. Generally, PVA grades with high degrees of hydrolysis have a lower solubility in water and are more difficult to crystallize.

In one embodiment, the polyvinyl alcohol of the present disclosure has a hydrolysis value of at least 60%, preferably at least 65%, preferably at least 70%, preferably at least 75%, preferably at least 80%, preferably at least 85%, preferably at least 90%, preferably at least 91%, preferably at least 92%, preferably at least 93%, preferably at least 94%, preferably at least 95%, preferably at least 96%, preferably at least 97%, preferably at least 98%, preferably at least 99%, where a value of 100% is complete hydrolysis and 0% is no hydrolysis.

Polyvinyl alcohol is produced by free radical polymerization and subsequent hydrolysis resulting in a wide molecular weight distribution. In one embodiment, the polyvinyl alcohol of the present disclosure has an average molecular weight of 5-200 kDa, preferably 10-150 kDa, preferably 10-100 kDa, preferably 10-75 kDa, more preferably 10-50 kDa, preferably 20-35 kDa.

Dispersity is a measure of the heterogeneity of sizes of molecules or particles in a mixture. The polydispersity index (PDI or heterogeneity index) is a measure of the distribution of molecular mass in a given polymer sample. The PDI is calculated as the weight average molecular weight divided by the number average molecular weight. Typically, dispersities vary based on the mechanism of polymerization and can be affected by a variety of reaction conditions such as reactant ratios, how close the polymerization went to completion, etc. Generally, a decreasing molecular weight distribution increases water solubility and increase flexibility. It can further affect properties of PVA including crystallizability, adhesion, mechanical strength and diffusivity. In one embodiment, the polyvinyl alcohol of the present disclosure has a PDI of up to 6, preferably up to 5, preferably

up to 3, preferably up to 2.5, preferably up to 2, preferably up to 1.5, preferably up to 1.25.

The degree of polymerization (DP) is defined as the number of monomeric units in a macromolecule or polymer. In one embodiment, the polyvinyl alcohol of the present disclosure has a degree of polymerization of 100-2500, preferably 100-1500, preferably 100-750, preferably 100-300.

General grades of polyvinyl alcohol include ultra-low viscosity (DP<300 and average molecular weight<23 kDa), low viscosity (DP=350-650 and average molecular weight=31-50 kDa), medium viscosity (DP=1000-1500 and average molecular weight=85-124 kDa) and high viscosity (DP=1600-2200 and average molecular weight=146-186 kDa). In the present disclosure, polyvinyl alcohol may refer to PVA that is ultra-low viscosity, low viscosity, medium viscosity, high viscosity or mixtures thereof.

It is envisioned that other polymeric materials may be used in lieu of polyvinyl alcohol as the polymer matrix of the nanocomposite film of the present disclosure. Although the selection of a polymer is not viewed as particularly limiting, the polarity of the polymer should be compatible with the conductive nanofiller. Suitable polymers may be selected from the group including, but not limited to, polyacrylates, acrylics, poly(acrylic acid), poly(acrylonitrile), poly(2-hydroxyethylmethacrylate), sodium polyacrylate, ethylene glycol dimethacrylate, polystyrenes, high impact polystyrene, poly(vinyl pyridine), poly(methyl acrylate), polymethacrylates, poly(methyl methacrylate), polychloroprene, polyacrylamide, poly(N-isopropylacrylamide), poly(tetrafluoroethylene) (PTFE), poly(N-vinyl pyrrolidone), poly(vinyl pyrrolidinone), poly(vinyl pyridine), polyethylenes, low-density poly(ethylene), high-density poly(ethylene), chlorinated polyethylene (CPD), poly(propylene), poly (isobutylene), poly(butylene), polyvinyl chlorides (PVC), polyvinyl chloride acetate, polyacrylonitriles, poly(ethyl acetate), poly(vinyl acetate), polyvinylacetates, polyvinyl acetate phthalate, ethylene vinyl acetates, poly(ethylene glycol), polyphenylene ethers, poly(ethylene vinyl alcohol), poly(vinylidene fluoride), poly(p-phenylenevinylene), poly (benzoxazole), polyphenylenebenzobisoxazole (PBO), polyaryletherketones, poly(ether ether ketones), polyphenylenesulfides, polyamide imides, polyarylates, polyarylsulphones, poly(styrene-co-acrylonitrile), ethyl-vinyl-alcohol copolymers, copolymers of ethylene and 1-alkenes, polybutene-1, polymethylpentene, amorphous poly-alpha-olefins (APAO), terephthalates, polyacetylene, polyethylene oxides, polycycloolefins, polyisoprenes, polystyrene-polyisoprene diblock copolymers, polyamides, poly (ethylene terephthalate), poly(trimethylene terephthalate), poly(butylene terephthalate), polycarbonates, polychlorotrifluoroethylene, polyvinyldifluoride, polyperfluoroalkoxy, poly(ethylene oxide), ethylene oxide copolymers, poly(ethylene imine), poly(dimethyl siloxane), silcones, fluorosilicones, fluoropolymers, polybutadienes, butadiene copolymers, epoxidized natural rubbers, epoxy polymer resins, poly (cis-1,4-isoprene), poly (trans-1,4-isoprene), viton, phenolic resins, acrylic resins, vinylacetate resins, polyurethanes, polyurethane-urea, thermosetting polyimides, thermoplastic polyimides, poly(amic acid), polysulfones, polyetherimides, polyethersulfones, chlorosulfonates, polyoxymethylene, polyphenylene oxide, polyphenylenes, perfluorinatedpolyethylenepropylene, polyvinylidene chloride, fluoropoly(ether-imide), polyolefins, aromatic polyamides (Aramid, para-aramid), polyesters, conducting and conjugated polymers, liquid crystal polymers, liquid crystalline polyesters, vectran, biodegradable thermoplastic polyesters

and their copolymers, thermosetting polyesters, unsaturated polyesters, acetals, fluorinated elastomers, rubbers, styrene butadiene rubbers, bismaleimides, copolymer rubbers, styrene-isoprene-styrenes, styrene-butadiene-styrenes, ethylene-propylene, ethylene-propylene-diene monomers (EPDM), nitrile-butadienes, acrylonitrile butadiene styrene (ABS), polyethylene/acrylonitrile butadiene styrene, polycarbonate/acrylonitrile butadiene styrene, nylons, thermoplastic continuous and discontinuous fiber composites, thermosetting continuous and discontinuous fiber composites, specialty polymers, etc. and blends, mixtures, alloys and copolymers thereof.

Intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity. They can have metallic conductivity or can be semiconductors. They offer high electrical conductivity but do not show similar mechanical properties to other available polymers. Their electrical properties can be fine-tuned using the methods of organic synthesis and advanced dispersion techniques.

In one embodiment, it is envisioned that the polymer matrix of the nanocomposite film may be adapted to incorporate an intrinsically conducting polymer. Examples of intrinsically conducting polymers include, but are not limited to, poly(fluorene)s, polyphenylenes, polypyrenes, polyazulenes, polynaphthalenes, poly(acetylene)s (PAC), Poly(p-phenylene vinylene) (PPV), poly(pyrrole)s (PPY), polycarbazoles, polyindoles, polyazepines, polyanilines (PANI), poly(thiophene)s (PT), poly(3,4-ethylenedioxythiophene) (PEDOT), poly(p-phenylene sulfide) (PPS) and copolymers and mixtures thereof.

In one embodiment, the polymer matrix is envisioned to be comprised of polyvinyl alcohol copolymers including, but not limited to, poly(vinyl alcohol-co-ethylene) ethylene, poly(acrylic acid)-co-poly(vinyl alcohol) copolymer, poly (vinyl butyral)-co-poly(vinyl alcohol copolymer, poly(vinyl acetate)-co-poly(vinyl alcohol) copolymer, poly(vinyl chloride)-co-poly(vinyl alcohol) and mixtures thereof.

In one embodiment, the polymer matrix is envisioned to be comprised of polyvinyl alcohol doped with additives including, but no limited to, crosslinkers, defoamers, dispersants, biocides and plasticizers.

In one embodiment, the conductive nanofiller is an inexpensive carbonaceous nanomaterial such as carbon black (e.g., furnace black and Ketjen black), active carbon, carbon nanorods, carbon nanotubes, carbon fibers, graphene, graphite, expandable graphite, graphene oxide, exfoliated graphite nanoplatelets, thermally reduced graphene oxide, chemically reduced graphene oxide and mixtures thereof, more preferably graphene, graphite, graphene oxide and mixtures thereof, most preferably graphene.

In a preferred embodiment, the conductive nanofiller is graphene. Graphene is an allotrope of carbon in the form of a two-dimensional, atomic-scale hexagonal lattice in which one atom forms each vertex. Graphene is approximately 200 times stronger than steel by weight and conducts heat and electricity with great efficiency. It is the basic structural element of other allotropes including graphite, charcoal, carbon nanotubes and fullerenes. Carbon nanotubes are formed by rolling up a graphene sheets into a tubular structure and graphite is formed by stacking multiple graphene sheets.

Structurally, graphene is a crystalline allotrope of carbon with 2-dimensional properties. As used herein, graphene is a sheet of six membered carbon rings that do not form a closed surface. Its carbon atoms are densely packed in a regular atomic-scale "chicken wire" (hexagonal) pattern. Each atom has four bonds, one σ-bond with each of its three

neighbors and one π-bond that is oriented out of the plane. Graphene's hexagonal lattice can be regarded as two interleaving triangular lattices.

Graphene's stability is due to its tightly packed carbon atoms and each carbon atom in a graphene sheet having a sp^2 orbital hybridization and delocalized electrons present at opposite surfaces of the graphene sheet. The sp^2 hybridization is a combination of orbitals S, P_x and P_y that constitute the σ-bond, the final P_z electron makes up the π-bond. The π-bonds hybridize together to form the π-band and the π*-band. These bands are responsible for most of graphene's notable electronic properties, via the half-filled band that permits free-moving electrons. Graphene is a zero-gap semiconductor. Graphene is also the only form of carbon (or solid material) in which every atom is available for chemical reaction from two sides (due to the 2D structure).

In one embodiment, the graphene conductive nanofiller of the present disclosure may be present as a one-atom thick (~0.33 nm) single layer, or monolayer. As used herein the monolayer is termed a "nanosheet". In another embodiment, the graphene may be present as a bilayer (two atom thick layer) or trilayer (three atom thick layer). In another embodiment, the graphene of the present disclosure may be present as several stacked graphene layers. Thus, in one embodiment the graphene layer may have a thickness greater than one atom and up to 200 atoms, preferably up to 100 atoms, preferably up to 50 atoms, preferably up to 10 atoms, preferably up to 5 atoms, preferably up to 4 atoms, preferably up to 3 atoms.

In very basic terms graphene could be described as a single, one atom thick layer of the commonly found mineral graphite; as used herein "graphite" is essentially made up of hundreds, preferably thousands of layers of graphene. Graphene nanoplatelets have "platelet" morphology, meaning they have a very thin but wide aspect ratio. As used herein a "nanoplatelet" consists of several sheets of graphene with an overall thickness. In one embodiment, the graphene nanoplatelets overlap one another to form a multilayer structure. The graphene of the conductive nanofiller of the present disclosure may be nanosheet graphene, nanoplatelet graphene, and/or mixtures thereof.

Multilayer graphene is a material consisting of two or more layers of graphene. Multilayer graphene can exist in the AB, or Bernal-stacked form, where half of the atoms lie directly over the center of a hexagon in the lower graphene sheet, and half of the atoms lie over an atom. Multilayer graphene can also exist in the AA form in which the layers are exactly aligned. Multilayer graphene can also be found in a twisted configuration. The graphene of the conductive nanofiller of the present disclosure may be multilayer graphene in the AB form, the AA form, the twisted form and mixtures thereof.

In one embodiment, the graphene nanosheets or nanoplatelets of the present disclosure may have wrinkled and/or rippled morphologies. The height of these wrinkles or ripples from the basal plane of the graphene nanosheets or nanoplatelets may range from less than 0.25 nm to about 5 nm, preferably from 0.3-2.5 nm, preferably from 0.5-2 nm, preferably from 1-1.5 nm. The number and frequency of these wrinkles or ripples can vary depending on the chemical size and structure of the nanosheet or nanoplatelet. In another embodiment, the nanosheets or nanoplatelets may be substantially corrugated leading to substantially increased surface area relative to non-corrugated nanosheets or nanoplatelets of comparable size.

In one embodiment, the graphene nanosheets or nanoplatelets of the present disclosure may form sandwich struc-

tures such as a sandwich of graphene-polymer-graphene or polymer-graphene-polymer, and so on to more complex multilayer structures with repeating layers of graphene and polymer matrix.

In one embodiment, the graphene nanosheets or nanoplatelets of the present disclosure may be scrolled, forming multilayer micron-sized cylindrical structures with two open ends and a hollow center resembling single-walled or multi-walled carbon nanotubes. In one embodiment, these structures have an outer diameter of 0.5-5 μm, preferably 1-4 μm, preferably 2-3 μm. In one embodiment, these structures have a length of 3-40 μm, preferably 5-30 μm, preferably 10-20 μm.

In one embodiment, the inter-planar distance of the graphene is less than 10 Å, preferably less than 7.5 Å, preferably less than 5 Å, preferably less than 4 Å, preferably less than 3 Å, preferably less than 2.5 Å, preferably less than 2 Å, preferably less than 1.5 Å, preferably less than 1 Å.

In one embodiment, the graphene of the present disclosure is in the form of nanoplatelets having an average thickness of 0.5-300 nm, preferably 1-250 nm, preferably 10-200 nm, preferably 20-150 nm, preferably 25-125 nm, preferably 50-100 nm.

In one embodiment, the graphene of the present disclosure is in the form of nanoplatelets having an average diameter or width of 1-75 μm, preferably 2.5-50 μm, preferably 5-45 μm, preferably 10-40 μm, preferably 20-30 μm.

In one embodiment, the graphene of the present disclosure is in the form of nanoplatelets having an aspect ratio of 200-2000, preferably 500-1500, more preferably 900-1200.

In one embodiment, the graphene of the present disclosure is in the form of nanoplatelets having a surface area in the range of 10-2500 nm^2, preferably 25-2000 nm^2, more preferably 50-1500 nm^2, more preferably 75-1250 nm^2, more preferably 100-1000 nm^2, more preferably 150-750 nm^2, or more preferably 200-500 nm^2.

In one embodiment, the graphene of the present disclosure is in the form of nanoplatelets having a specific surface area of 2.5-750 m^2/g, preferably 5-500 m^2/g, preferably 7.5-300 m^2/g, preferably 10-150 m^2/g, preferably 12-120 m^2/g, preferably 15-100 m^2/g.

In one embodiment, the graphene comprising the conductive nanofiller of the present disclosure has not been chemically modified, it is pristine graphene and a pure carbonaceous material having a purity of greater than 90%, preferably greater than 95%, preferably greater than 96%, preferably greater than 97%, preferably greater than 98%, preferably greater than 99%. In one embodiment, the graphene comprising the conductive nanofiller of the present disclosure has an oxygen content of less than 5%, preferably less than 4%, preferably less than 3%, preferably less than 2%, preferably less than 1%. In one embodiment, the graphene comprising the conductive nanofiller of the present disclosure has a C/O ratio of at least 10, preferably at least 20, preferably at least 30, preferably at least 40, preferably at least 50, preferably at least 75, preferably at least 100, preferably at least 150, preferably at least 200.

In one embodiment, the graphene comprising the conductive nanofiller of the present disclosure may be chemically modified; graphene is commonly modified with nitrogen and oxygen containing functional groups (e.g. graphene oxide). Exposed carbon on the edges of nanosheets or nanoplatelets often reacts with the atmosphere to form hydroxyls, carboxyls, lactones, pyrones, alcohols, carbonyls, imines and/or amines. These modifications may be covalent, non-covalent or mixtures thereof. Examples of functional groups on graphene include, but are not limited to, alcoholic, carbox-

ylic, aldehydic, ketonic and esteric oxygenated functional groups. Alternatively, the graphene may be chemically modified with amine or imine functionality. Chemical functionalization of the graphene may aid the manufacturing of the graphene polymer nanocomposite or improve the interface between the conductive nanofiller and the polymer matrix.

In one embodiment, the graphene comprising the conductive nanofiller of the present invention has been chemically modified such that it has a C/O ratio of less than 10, preferably less than 5, preferably less than 4, preferably less than 3, preferably less than 2. In another embodiment, the graphene comprising the conductive nanofiller of the present invention has been chemically modified such that it has a C/N ratio of less than 50, preferably less than 40, preferably less than 30, preferably less than 20, preferably less than 20.

In one embodiment, it is envisaged that the present invention may be adapted to incorporate nanoscale metals as the conductive nanofiller. Examples of possible metals include, but are not limited to, silver, gold, copper, nickel, iron, aluminum zinc, palladium, platinum, magnesium, zirconium, titanium, vanadium, rhodium, rhenium, uranium, silicon, molybdenum, thorium, chromium, manganese, cerium, germanium, tantalum, lead, cadmium, calcium, antimony, tin, bismuth, cobalt, tungsten, indium, silicone, brass, bronze, white brass, stainless steel and alloys or mixtures thereof.

In one embodiment, it is envisaged that the present invention may be adapted to incorporate nanoscale metal oxides as the conductive nanofiller. Examples of possible metal oxides include, but are not limited to oxides of iron, copper, zinc, magnesium, vanadium, nickel, rhodium, rhenium, molybdenum, thorium, chromium, manganese, cerium, silver, lead, cadmium, calcium, antimony, tin, bismuth, cobalt, tungsten, titanium dioxide (anatase, rutile), alumina (Al_2O_3), antimony-tin-oxide (ATO), silica (diatomite, pyrogenic silica, silica fume), ruthenium dioxide (RuO_2), bismuth ruthenate ($Bi_2Ru_2O_7$), bismuth iridate ($Bi_2Ir_2O_7$), indium oxide (In_2O_3), lanthanum chromite ($LaCr_2O_4$), zirconia (ZrO_2), titania, iron oxide, silica-alumina, mica, ferrite and mixtures thereof.

In another embodiment, the conductive nanofiller may be additional inorganic materials such as boehmite, a mineral aluminum oxide hydroxide (γ-AlO(OH)) orthorhombic dipyramidal crystal. It can be obtained naturally or from chemical synthesis from saturated solutions. In another embodiment, the conductive nanofiller may be metal carbonates including, but not limited to magnesium carbonate, potassium carbonate, sodium carbonate, barium carbonate, calcium carbonate and mixtures thereof.

In one embodiment, it is envisaged that the present invention may be adapted to incorporate nanoscale fillers of natural or synthetic clays as well as phosphates of transition metals as the conductive nanofiller. The nanoscale clays are classified according to their crystalline structures and also to the quantity and position of the ions within their simplest atomic geometric pattern. The most widely used nanoscale clays are phyllosilicates (smectites) having a shell-shaped crystalline structure with nanometer thickness but also include polysilicates and double lamellar hydroxides. Examples of possible nanoclays include, but are not limited to, montmorillonite (MMT), kaolinite, smectite (Talc, Mica, MMT), sepiolite, chlorite, saponite, bentonite, kenyaite, magadiite, kanemite, ilerite, silhydrite, zeolite, fluorohectorite, hydrotalcite and mixtures thereof.

In one embodiment, it is envisaged that the present invention may be adapted to include nanoscale ceramics as

the conductive nanofiller. Representative examples of ceramics include carbides such as silicon carbide (SiC), chromium carbide (Cr_3C_2), titanium carbide (TiC), zirconium carbide (ZrC), boron carbide (B_4C) and diamond (C), nitrides such as silicon nitrides (SiN, Si_3N_4), boron nitride (BN), zirconium nitride (ZrN), niobium nitride (NbN), and titanium nitride (TiN), borides such as titanium boride (TiB), zirconium boride (ZrB), tantalum boride (TaB), vanadium boride (VB_2), and lanthanum boride (LaB_6) and silicides such as titanium silicide (TiSi), tantalum silicide (TaSi), molybdenum silicide (MoSi), and tungsten silicide (WSi_2).

In one embodiment, it is envisaged that the present invention may be adapted to include nanoscale electroceramics as the conductive nanofiller. Representative examples of electroceramics include zirconium barium titanate, strontium titanate (ST), calcium titanate (CT), magnesium titanate (MT), calcium magnesium titanate (CMT), zinc titanate (ZT), lanthanum titanate (TLT), lithium lanthanum titanate (LLT), neodymium titanate (TNT), barium zirconate (BZ), calcium zirconate (CZ), lead magnesium niobate (PMN), lead zinc niobate (PZN), lithium niobate (LN), barium stannate (BS), calcium stannate (CS), layered silicates, magnesium aluminum silicate, magnesium silicate, barium tantalite, titanium dioxide, niobium oxide, sapphire, beryllium oxide, barium titanate, zirconia, silica, zirconium tin titanate and mixtures thereof.

In one embodiment, it is envisaged that the present invention may be adapted to include nanoscale silsesquioxanes as the conductive nanofiller. A silsesquioxane is an organosilicon compound with the empirical formula $RSiO_{3/2}$ where R is hydrogen or an alkyl, alkene, aryl, arylene or organo-functional group. Silsesquioxanes can have a cage-like structure, most commonly in the form of a cube, hexagonal prism, octagonal prism, decagonal prism, dodecagonal prism, or opened cage-like structure. The high three-dimensional symmetry and nanometer size make silsesquioxanes building blocks for nanocomposites. The diversity of possible functional groups along with their controlled orientation in three-dimensional space allows for highly tailored nanometer-by-nanometer construction in all three dimensions. Examples of possible silsesquioxanes include, but are not limited to, polyhedral oligosilsesquioxanes (POSS), octasilsesquioxanes of the $[ROSiO_{1.5}]_8$ type and its polymeric derivatives and the $[R\text{-phenylSiO}_{1.5}]_8$ type and its polymeric derivatives.

In one embodiment, the nanocomposite film comprises up 0.01-0.25% conductive nanofiller by weight relative to the total weight of the nanocomposite film, preferably 0.01-0.3%, preferably 0.01-0.35%, preferably 0.01-0.4%, preferably 0.01-0.45%, preferably 0.01-0.49% by weight relative to the total weight of the nanocomposite film.

In one embodiment, the nanocomposite film has a first surface that is insulating and a second surface that is insulating. The first surface is insulating and has a first resistivity of greater than 10^8 ohm·cm^2, preferably greater than 1.25×10^8, preferably greater than 1.5×10^8, preferably greater than 1.75×10^8, preferably greater than 2.0×10^8, preferably greater than 2.5×10^8, preferably greater than 3×10^8, preferably greater than 3.5×10^8, preferably greater than 4.0×10^8, preferably greater than 5.0×10^8 ohm·cm^2. The second surface is insulating and has a second resistivity of greater than 10^8 ohm·cm^2, preferably greater than 1.25×10^8, preferably greater than 1.5×10^8, preferably greater than 1.75×10^8, preferably greater than 2.0×10^8, preferably greater than 2.5×10^8, preferably greater than 3×10^8, preferably greater than 3.5×10^8, preferably greater than 4.0×10^8, preferably greater than 5.0×10^8 ohm·cm^2.

In one embodiment, the nanocomposite film comprises from 0.5-1.0% of conductive nanofiller by weight relative to the total weight of the nanocomposite film, preferably 0.5-1.25%, preferably 0.5-1.5%, preferably 0.5-1.75%, preferably 0.5-2.0%, preferably 0.5-2.25%, preferably 0.5-2.5%, preferably 0.5-2.75%, preferably 0.5-2.9%, preferably 0.5-2.995 by weight relative to the total weight of the nanocomposite film.

In one embodiment, the nanocomposite film has a first surface that is insulating and a second surface that is antistatic. The first surface is insulating and has a first resistivity of greater than 10^8 ohm·cm^2, preferably greater than 1.25×10^8, preferably greater than 1.5×10^8, preferably greater than 1.75×10^8, preferably greater than 2.0×10^8, preferably greater than 2.5×10^8, preferably greater than 3×10^8, preferably greater than 3.5×10^8, preferably greater than 4.0×10^8, preferably greater than 5.0×10^8 ohm·cm^2. The second surface is antistatic and has a second resistivity of 10^4-10^8 ohm·cm^2, preferably 10^4-10^7, preferably 10^4-10^6, preferably 10^4-7.5×10^5, preferably 10^4-5.0×10^5, preferably 10^4-2.5×10^5, preferably 10^4-10^5, preferably 10^4-0.5×10^5, preferably 10^4-0.25×10^5 ohm·cm^2.

In one embodiment, the nanocomposite film comprises from 3-10% conductive nanofiller by weight relative to the total weight of the nanocomposite film, preferably 3-5%, preferably 3-7%, preferably 3-8%, preferably 3-9%, preferably 3-12%, preferably 3-15%, preferably 3-20%, preferably 3-25% by weight relative to the total weight of the nanocomposite film.

In one embodiment, the nanocomposite film has a first surface that is insulating and a second surface that is semiconducting and/or conducting. The first surface is insulating and has a first resistivity of greater than 10^8 ohm·cm^2, preferably greater than 1.25×10^8, preferably greater than 1.5×10^8, preferably greater than 1.75×10^8, preferably greater than 2.0×10^8, preferably greater than 2.5×10^8, preferably greater than 3×10^8, preferably greater than 3.5×10^8, preferably greater than 4.0×10^8, preferably greater than 5.0×10^8 ohm·cm^2. The second surface is semiconducting and/or conducting and has a second resistivity of less than 10^4 ohm·cm^2, preferably less than 7.5×10^3, preferably less than 5.0×10^3, preferably less than 4.0×10^3, preferably less than 3.5×10^3, preferably less than 3.0×10^3, preferably less than 2.5×10^3, preferably less than 2.0×10^3, preferably less than 1.5×10^3, preferably less than 1.0×10^3, preferably less than 0.75×10^3, preferably less than 0.5×10^3 ohm·cm^2.

Thus, the nanocomposite film of the present disclosure may be insulating in the bulk or at one surface but additionally present an antistatic, semiconducting and/or conducting surface. Thus, a single material is presented that can fulfill the function of both an electrical insulator and an electrical semiconductor and/or conductor depending on which surface is engaged.

According to a second aspect, the present disclosure relates to a process for forming the nanocomposite films of the present disclosure, in one or more of their embodiments.

In a preferred embodiment, the nanocomposite film of the present disclosure is formed by a solution processing or solution mixing and casting technique. The process is described as wet chemistry and is considered simple and cost effective compared to other processes for manufacturing polymer nanocomposites. In general, solution processing refers to the dispersion of conductive nanofiller into a solvent followed by mixing with a polymer solution and subsequent vaporization of the solvent to form the desired nanocomposite.

In one embodiment, the solution processing begins with dispersion of the conductive nanofiller into a liquid solution by energetic mixing. The certain amount of conductive nanofiller is determined by the desired weight percent of the final nanocomposite. In one embodiment, the ratio of polymer matrix to conductive nanofiller may be 85:1, 90:1, 93:1, 95:1, 97:1, 99:1, 99.5:1, 99.75:1. This mixing may include, but is not limited to, mechanical mixing, magnetic agitation, mild sonication, high-energy ultrasonication, shear mixing, refluxing and mixtures thereof. The process of mixing to form a stable dispersion may last as little as 2 hours, preferably 1.5 hours, preferably 1 hour, preferably 30 minutes, preferably 15 minutes, preferably 10 minutes, preferably 5 minutes. In one embodiment, the dispersion of nanofiller may occur directly in a polymeric solution, in another embodiment the nanofiller is dispersed in a solvent and then mixed with an independent polymer solution that may be in the same solvent or a different solvent.

In one embodiment, once combined in a reaction mixture the dispersed conductive nanofiller solution and the polymer solution are further mixed by the means discussed previously, preferably heating, magnetic agitation and ultrasonication. In one embodiment the reaction mixture is mixed at elevated temperature of at least 40° C., preferably at least 60° C., preferably at least 70° C., preferably at least 80° C. The process of mixing the reaction mixture may last as little as 2 hours, preferably 1.5 hours, preferably 1 hour, preferably 30 minutes, preferably 15 minutes. In one embodiment, following the mixing the reaction mixture is degassed to remove any traces of air from the solution with inert gas. The process of degassing may last as little as 2 min, preferably 5 min, preferably 10 min, preferably 15 min. Finally, the mixture is poured on a leveled flat surface and allowed to dry at room temperature. The dried films may then be peeled from the surface they were poured and cast on and kept in a desiccator to avoid moisture uptake. In one embodiment, the nanocomposite films are cast and dried in plastic petri dishes. In one embodiment, the drying is done at elevated temperature up to 200° C., preferably up to 150° C., preferably up to 100° C., preferably up to 75° C., preferably up to 50° C. The drying time may take up to 24 hours, preferably up to 12 hours, preferably up to 8 hours, preferably up to 4 hours, preferably up to 2 hours.

The nature of the conductive nanofiller/polymer ratio and fabrication conditions including, but not limited to temperatures, sonications, step durations and casting and drying conditions are what allow for control of the size, shape and non-uniform dispersion of the conductive nanofiller in the nanocomposite film. Thus, variations in the above process give rise to a nanocomposite film comprising a first surface and a second surface. The first surface has a first content of conductive nanofiller and a first resistivity. The second surface has a second content of conductive nanofiller and a second resistivity. The second content of conductive nanofiller is greater than or equal to the first content of conductive nanofiller, and the second resistivity is less than or equal to the first resistivity.

In one embodiment, the polymerization by solution processing is carried out in a liquid solvent that may include polar protic solvents, aprotic polar solvents and non-polar solvents. Suitable polar protic solvents may include, but are not limited to, water, nitromethane, and short chain alcohols such as methanol, ethanol, propanol, isopropanol, butanol of the like and mixtures thereof. Suitable aprotic polar solvents may include, but are not limited to, propylene carbonate, ethylene carbonate, butyrolactone, acetonitrile, benzonitrile, nitromethane, nitrobenzene, sulfolane, dimethylformamide,

N-methylpyrrolidone or the like and mixtures thereof. Suitable non-polar solvents may include, but are not limited to, cyclohexane, octane, heptane, hexane, benzene, toluene, xylene, methylene chloride, carbon tetrachloride, diethyl ether or the like and mixtures thereof. In one embodiment, co-solvents may also be used. In a most preferred embodiment, the liquid solvent is water.

In one embodiment, the reaction mixture of the present process may contain one or more additional additives to change the properties of the nanocomposites and/or to improve the process of producing the nanocomposites. Exemplary additives include, but are not limited to, surfactants, antifoaming agents or defoamers, a scale inhibitor, a corrosion inhibitor, a colorant, a thermal stabilizer, a dopant, a coolant additive, a polymerization catalyst, a hardener, a Lewis base, a plasticizer and mixtures thereof.

In one embodiment, the nanocomposite film may further undergo one or more manufacturing steps after formation to instill any desired properties. Techniques or processes including, but not limited to, vulcanization, grafting, cross-linking, injection molding, hot pressing, drawing, extrusion, autoclaving, annealing, heat treating, sintering, compression molding, machining, welding, adhesively bonding, thermoforming, coating, vacuum forming, blow molding, stretch blow molding, transfer molding, calendaring, compounding, orienting, tape laying with in situ consolidation, diaphragm forming, rotational molding, centrifugal molding, fiber spinning, filament winding, foam blowing, pultruding and the like are considered to be within the scope of the present method.

In another embodiment, the polymer nanocomposite film of the present disclosure is formed by in situ polymerization. In general, the conductive nanofiller is mixed with monomers or pre-polymers and then the nanocomposite is formed by polymerizing the monomers or pre-polymers. This method may further encompass the use of metallocene-based catalyst, anchoring agents such as methylaluminoxane and/or a hardener. This polymerization process is usually accompanied by a viscosity increase that hinders manipulation and limits load fraction. Additionally, solvents may be necessary and may need to be removed, similarly to solution processing.

In another embodiment, the polymer nanocomposite film of the present disclosure is formed by melt blending. This method is generally applied to polymers that are insoluble and is particularly useful for dealing with thermoplastic polymers. The technique capitalizes on the fact that thermoplastic polymers soften when heated. Amorphous polymers are heated above their glass transition temperature and semi-crystalline polymers are heated above their melt temperature to induce sufficient softening. Conductive nanofiller can then be mixed into the melt by conventional blending equipment such as shear mixing or a twin screw extruder and bulk samples can be further fabricated by techniques such as compression molding, injection molding, and/or extrusion. In other embodiments, the polymer nanocomposite film of the present disclosure is further envisioned to be produced by novel methods including, but not limited to, solid-state mechanochemical pulverization, coagulation spinning and/or latex fabrication methods.

In a preferred embodiment, the conductive nanofiller is graphene and the polymer matrix is poly(vinyl alcohol). In one embodiment, the graphene can be prepared from exfoliation of graphite. As used herein, "exfoliation" refers to cleavage or coming apart of a material shed from a surface in scales or layers. The exfoliation may be by mechanical cleavage means such as adhesive tape, shearing or wedge

based mechanical exfoliation. The exfoliation may also be by direct sonication cleavage such as solvent-aided sonication, solvent/surfactant aided sonication and immiscible liquid aided sonication. In one embodiment, the graphene can be prepared from graphite oxide or graphene oxide via thermal (~2000° C./s) or chemical (hydrazine) reduction followed by or preceded by exfoliation.

In another embodiment, the graphene may be produced by epitaxy. Epitaxy refers to the deposition of a crystalline overlayer on a crystalline substrate, ideally coupled weakly enough to retain the two dimensional electronic band structure of isolated graphene. Suitable substrates include, but are not limited to silicon carbide, metals such as ruthenium, iridium, nickel or copper. The graphene conductive nanofiller of the present disclosure is envisioned to be produced by a variety of techniques including, but not limited to, the sugar method, sodium ethoxide pyrolysis, roll-to-roll manufacturing, silicon/germanium/hydrogen chemical vapor deposition, nanotube slicing, carbon dioxide reduction, spin coating, supersonic spray, intercalation, CO_2 infrared laser, and microwave assisted oxidation.

In another embodiment, the nanocomposite film of the present disclosure may be formed by methods requiring a substrate, typically glass or plastic. Such methods include, but are not limited to chemical vapor deposition (CVD), preferably microwave-assisted CVD, and spin coating.

Chemical vapor deposition (CVD) is a chemical process used to produce high quality, high-performance solid thin film materials. In typical CVD, a substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber. CVD is practiced in a variety of formats differing primarily in the means by which chemical reactions are initiated. CVD can be classified by the physical characteristics of the vapor such as aerosol assisted CVD or direct liquid injection CVD, plasma methods such as microwave plasma-assisted CVD, plasma-enhanced CVD or remote plasma-enhanced CVD, as well as atomic-layer CVD, combustion chemical vapor deposition, hot filament CVD, hybrid physical-chemical vapor deposition, metalorganic chemical vapor deposition, rapid thermal CVD, vapor-phase epitaxy, and photo-initiated CVD. In one embodiment, the nanocomposite film of the present disclosure may be formed by chemical vapor deposition in any of its forms using a glass or plastic substrate.

Spin coating is a procedure used to deposit uniform thin films to flat substrates. A small amount of coating material is applied to the center of a substrate which is either spinning at low speed or not spinning at all. The substrate is then rotated at high speed in order to spread the coating material by centrifugal force. Rotation is continued while the fluid spins off the edges of the substrate, until the desired thickness of the film is achieved. The applied solvent is usually volatile, and simultaneously evaporates. Thus, the higher the angular speed of spinning, the thinner the film. The thickness of the film also depends on the viscosity and concentration of the solution. In one embodiment, the nanocomposite film of the present disclosure may be formed by spin coating in any of its forms using a glass or plastic substrate.

According to a third aspect, the present disclosure relates to an electrical or electronic device including the nanocomposite films of the present disclosure, in one or more of their embodiments.

In one embodiment, the electrical or electronic device is covered by the nanocomposite film by attaching the free-standing film to the device by any reasonable manner. The

nanocomposite may be attached through surface coating interaction (e.g. glued, tacked, cemented, pasted, etc.), attached by highly connected or integral interactions (e.g. melted together, fused, amalgamated, etc.), or sandwiched between a plurality of electronic components of the device. In another embodiment, the electrical or electronic device is covered by the nanocomposite film by first applying the conductive nanofiller/polymer reaction mixture to the device and then forming the nanocomposite on the device by drying. In another embodiment, the electrical device is covered by, attached to, wrapped or enclosed by a metal or alloy or ceramic substrate on which the nanocomposite is disposed.

In one embodiment, the nanocomposite film of the present disclosure may be transparent and find use as a transparent conductive film in photovoltaic cells, liquid crystal displays and touch panel devices. In another embodiment, the unique non-uniform electrical storage characteristics of the nanocomposite film of the present disclosure may find use in supercapacitors, Li—O_2 batteries, or Li-ion batteries.

In one embodiment, the nanocomposite film of the present disclosure is envisioned to find use as an antistatic agent or electrostatic discharge material. An antistatic agent is a compound used for the treatment of materials or their surfaces in order to reduce or eliminate the buildup of static electricity. The role of the antistatic agent is to make the surface of the material itself slightly conductive. Antistatic devices reduce static electricity that can damage electrical components such as computer hard drives, cause bodily injury, or ignite flammable liquids and gases.

Exemplary non-limiting applications of the nanocomposite film as an antistatic agent or component of an antistatic device include, but are not limited to, antistatic bags used to contain devices, such as graphics cards or hard disk drives, often during transport, antistatic garments such as gloves or shoes used in many industries such as electronics, communication, telecommunication and defense applications, antistatic mats, antistatic straps and antistatic bars used to ground many sensitive processes and systems.

In one embodiment, the nanocomposite film of the present disclosure is envisioned to find use as an electromagnetic shielding material. Electromagnetic (EM) shielding is the practice of reducing the electromagnetic field in a space by blocking the field with barriers made of conductive materials. Shielding is typically applied to enclosures for isolating electronic devices from the "outside world" and cables to isolate wire from the environment through which the cable runs. The nanocomposite film of the present disclosure may completely enclose an electronic product or a portion of that product and prevent the EM emission from an outside source from deteriorating its electronic performance. Conversely, it may also be used to prevent an external susceptible (electronic items or living organisms) from internal emissions of an instruments's electronic circuitry. In one embodiment, the nanocomposite film of the present invention may be applied to plastics comprising sensitive electronic devices.

Exemplary non-limiting applications of the nanocomposite film as an electromagnetic shielding material include, but are not limited to, an EM shielding gasket, a shielded cable, protection of medical, laboratory and defense equipment from interfering signals including AM, FM, TV, emergency services, dispatch, pagers, cellular, ESMR and PCS, protection for computers and keyboards to prevent passive monitoring, and protection of secure data stored on RFID chips embedded in many devices.

The examples below are intended to further illustrate protocols for preparing and characterizing the nanocompos-

ite films of the present disclosure. Further, they are intended to illustrate assessing the electrical and conductive properties of these nanocomposite films, specifically resistivity. They are not intended to limit the scope of the claims.

Example 1

Chemicals

Polyvinyl alcohol (PVA) was purchased from Sigma Aldrich Company and utilized directly without further purification. Millipor MilliQ purified deionized water was used in all operations. Graphene (Grafen®-iGP) of 96-99% purity was procured from Grafen Chemical Industries Co., Turkey and utilized directly without any further treatment or purification in the embodiments described herein.

Example 2

Preparation of Nanocomposite Blends

Blends of polyvinyl alcohol (PVA) and graphene were prepared by means of a solution mixing and casting method. 3 g of PVA was completely dissolved in deionized water (40 mL) at 98° C. under 600 rpm. Then a certain amount of graphene, based on the formulations as shown in table 1, was added to 35 mL of deionized water.

TABLE 1

Formulations used in preparing the polyvinyl alcohol and graphene blends	
Sample	Amount of graphene (g)
PVA (control)	—
PVAG (0.25 wt. %)	0.0075
PVAG (0.5 wt. %)	0.015
PVAG (1.0 wt. %)	0.03
PVAG (3.0 wt. %)	0.09
PVAG (5.0 wt. %)	0.15
PVAG (7.0 wt. %)	0.21
PVAG (10.0 wt. %)	0.30

A stable dispersion of graphene in water was prepared by ultra-sonication using the Ultrasonicator Probe (Ultrasonica Q 700) at an amplitude of 30% for 15 minutes. After that, the dispersion of water and graphene was added to the PVA solution in water and stirring was continued for one hour with the use of a magnetic stirrer at 600 rpm and at a temperature of 80° C. The mixture was then degassed for 10 minutes to remove any traces of air from the solution. Finally, the mixture was poured into a plastic Petri dish placed on a leveled flat surface and allowed to dry at room temperature. The dried films of approximately 0.5 mm in thickness were carefully peeled off from the plastic Petri dish and kept in a desiccator to avoid moisture uptake.

Example 3

Characterization of Nanocomposite Blends

Field emission scanning electron microscopy (FESEM) images were taken using MIRA3 TESCAN field emission SEM. The samples were cryo-fractured using liquid nitrogen before testing. The cross section of samples was coated with platinum (5 nm thickness) to make the surface conductive. The electrical resistances of the samples were measured using a digital source meter (Model 2400 Series, Keithley Instruments, Inc.). The calculated results of the electrical resistivity are reported in table 2.

TABLE 2

Sample	Surface Resistivity ($\Omega \cdot cm^2$) Second Surface	Surface Resistivity ($\Omega \cdot cm^2$) First Surface
PVA (control)	>200 × 10⁶	>200 × 10⁶
PVAG (0.25 wt. %)	>200 × 10⁶	>200 × 10⁶
PVAG (0.5 wt. %)	95.195 × 10³	>200 × 10⁶
PVAG (1.0 wt. %)	12.562 × 10³	>200 × 10⁶
PVAG (3.0 wt. %)	3.575 × 10³	>200 × 10⁶
PVAG (5.0 wt. %)	2.416 × 10³	>200 × 10⁶
PVAG (7.0 wt. %)	1.416 × 10³	>200 × 10⁶
PVAG (10.0 wt. %)	0.913 × 10³	>200 × 10⁶

Resistance measurements of polyvinyl alcohol and graphene blends

Pure PVA films demonstrated one homogeneous phase while the PVA/graphene nanocomposite films demonstrated by FESEM two phases (layers) of PVA and graphene being formed. The effect of graphene loading on the electrical surface resistivity of PVA/graphene bionanocomposites is presented in table 2. The surface resistivity has been reported for both surfaces of the film, where the first surface has been considered as an "upper" surface and the other as a "bottom" surface relative to and depending on location at the time of casting the nanocomposite film. Interestingly, there is tremendous difference in surface resistivity between the second and first surface. The surface resistivity of the first surfaces falls under insulating at all loadings of graphene meaning the surface is insulating in nature. However, the electrical surface resistivity of the second surface is found to decrease with increasing graphene loading in the nanocomposite. It is seen that the resistivity of the composites transitions from insulating (10^8-10^{17} ohm·cm²) to semiconductive/conductive (below 10^4 ohm·cm²) through antistatic (10^4-10^8 ohm·cm²) depending on the loading of graphene.

Thus, depending on the graphene loading, one can generate composites with insulating-insulating surfaces (PVA control and 0.25 wt. % graphene composite), insulating-antistatic surfaces (0.50 wt. % and 1.0 wt. % composites) and insulating-semiconductive/conductive surfaces (3-10 wt. % composites). These types of composites have practical value due to their applicability in different electrical and electronic fields. The advantage of using these insulating-semiconducting materials is that they minimize the risk of an electrical shock due to one surface being insulating in nature.

Thus, the foregoing discussion discloses and describes merely exemplary embodiments of the present invention. As will be understood by those skilled in the art, the present invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. Accordingly, the disclosure of the present invention is intended to be illustrative, but not limiting of the scope of the invention, as well as other claims. The disclosure, including any readily discernible variants of the teachings herein, defines, in part, the scope of the foregoing claim terminology such that no inventive subject matter is dedicated to the public.

The invention claimed is:

1. A single layer nanocomposite film, the nanocomposite film formed by a process comprising:
   dispersing conductive nanofillers in a polymer solution,
   allowing a portion of the conductive nanofillers to settle, thus forming a mixture, and
   drying the mixture to form the nanocomposite film;

wherein the nanocomposite film comprises a first surface, a second surface, and a polymer matrix formed from drying of the polymer solution:
   wherein the polymer matrix contains the dispersed conductive nanofillers, and wherein the dispersed conductive nanofillers account for 0.01-0.25 weight percent of the nanocomposite film, and
   wherein the settled conductive nanofillers define an interface between the first and second surfaces;
   wherein the first surface has a first content of conductive nanofillers and a first product of electrical resistance and area, R·A, and
   wherein the second surface has a second content of conductive nanofillers and a second product of electrical resistance and area, R·A,
      wherein the second content of conductive nanofillers is greater than the first content of conductive nanofillers,
      wherein the second R·A is less than or equal to the first R·A.

2. The nanocomposite film of claim 1, wherein the nanocomposite film has an average thickness of 0.1-1.0 mm.

3. The nanocomposite film of claim 1, wherein the polymer matrix comprises polyvinyl alcohol.

4. The nanocomposite film of claim 1, wherein the conductive nanofillers are pristine graphene.

5. The nanocomposite film of claim 4, wherein the polymer matrix comprises polyvinyl alcohol.

6. The nanocomposite film of claim 4, wherein the pristine graphene is in the form of nanosheets having an average longest dimension of 1-75 μm and an average thickness of 0.5-300 nm or nanoplatelets having an average diameter of 1-75 μm and an average thickness of 0.5-300 nm.

7. The nanocomposite film of claim 1, wherein the first surface is insulating and the second surface is insulating.

8. The nanocomposite film of claim 1, wherein the first surface is insulating and has a first R·A of greater than 10^8 ohm·cm².

9. An electronic device comprising the nanocomposite film of claim 1, wherein the nanocomposite film is present in or on said electronic device.

10. A single layer nanocomposite film, the nanocomposite film formed by a process comprising:
   dispersing conductive nanofillers in a polymer solution,
   allowing a portion of the conductive nanofillers to settle, thus forming a mixture, and
   drying the mixture to form the nanocomposite film;
      wherein the nanocomposite film comprises a first surface, a second surface, and a polymer matrix formed from drying of the polymer solution:
      wherein the polymer matrix contains the dispersed conductive nanofillers, and
      wherein the settled conductive nanofillers define an interface between the first and second surfaces;
   a first surface having a first content of conductive nanofillers and a first product of electrical resistance and area, R·A, and
   a second surface having a second content of conductive nanofillers and a second product of electrical resistance and area, R·A,
   wherein the second content of conductive nanofillers is greater than the first content of conductive nanofillers,
   wherein the second R·A is less than or equal to the first R·A, and

wherein the second surface is insulating and has a second R·A of greater than 10^8 ohm·cm^2.

* * * * *